EFFECT OF STARCH AND SURFACTANT ON VISCOSITY OF BENTONITE SUSPENSION

Thesis submitted

By

ANSUPALLAV (111CH0091)

In partial fulfilment for the award of the Degree of

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Under the guidance of

Dr. SANTANU PARIA

Department of Chemical Engineering

National Institute Of Technology, Rourkela

Rourkela-769008, Orissa, India

National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"EFFECT OF STARCH AND SURFACTANT ON VISCOSITY OF BENTONITE SUSPENSION"** submitted by Ansupallav in partial fulfilments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree.

DATE: 9th June 2015

Dr. Santanu Paria

Dept. of Chemical Engineering

National Institute of Technology

Rourkela, Odisha-769008

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Date: 9th June 2015 ANSUPALLAV

Roll No: 111CH0091

Department of Chemical Engineering

National Institute of Technology, Rourkela.

ABSTRACT

The rheological behaviour of bentonite-water slurry has been studied along with the addition of corn starch and potato starch. The effects of solid concentration as well the effect of surfactant on the rheological behaviour of bentonite-water slurry were experimented. The changes in the flow properties of the modified bentonite-water slurry were studied by measuring the viscosity using a cone and plate viscometer. It was found that the viscosity of bentonite suspensions decreases with increasing shear rate depicting the pseudoplastic nature of the suspension. With the addition of starch the viscosity was found to be decreasing. The heating of the clay-starch slurry led to decreased values of viscosity. The viscosity values were found to be lowered by the addition of surfactant.

KEYWORDS: Viscosity, Starch, Clay, Surfactant, Rheology, Pseudoplastic

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CHAPTER1

INTRODUCTION

1. INTRODUCTION

Rheometry refers to a technique which is incorporated to determine the rheological nature of materials (fluid or solid). A viscometer is used to measure the viscosity of a fluid. Viscosities of those liquids which vary with flow conditions is measured by an instrument called rheometer.

1.1 Shear

Viscosity is an estimate of the resistance of a fluid to distortion by shear stress or tensile stress. The more is the friction between the layers of the fluid more is the force needed to produce the relative movement which is called shear [1]. Fluids having higher viscosity need more force to move than those with lower viscosity.

1.2 Shear Rate

When a fluid is flowing between a moving and a stationary plate, the shear rate-R is defined as the velocity gradient of the two plate dv/dx and its unit of measure is reciprocal second (sec^{-1}).

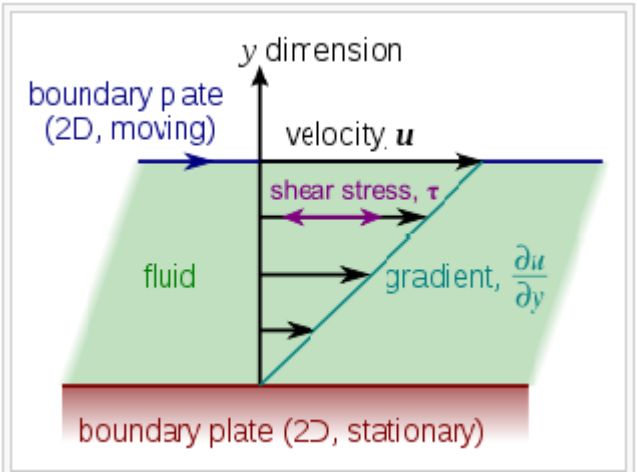


Fig.1.1: Movement of two plates over each other [14]

1.3 Shear Stress

The force per unit area parallel to the cross-section of the body producing the shearing action is called the shear stress-S and the unit of shear stress is N/m^2. Now viscosity can be defined as Shear Stress-S/Shear Rate-R. Its fundamental unit of measure is poise [1]. A shear stress of 1 dyne per 1 cm^2 required to produce a shear rate of $1s^{-1}$ equals a viscosity of 1 poise or 100 centipoise. 1 Pascal-sec equals to 10 poise.

1.4 Rheological classification of Fluids

Fluids are initially classified as Newtonian and Non-Newtonian depending on whether they follow Newton's law of viscosity or not. Non-Newtonian are classified as time-dependent or time-independent [14]. Fluids in which rheological behaviour depends only on shear stress are time independent. In time dependent fluids viscosity depends on amount of time for which stress has been applied to the fluid. These fluids possess both viscous and elastic behaviour and are called viscoelastic fluids.

The figures below show the relationship of shear stress S with rate of shear R and viscosity with varying rate of shear R for a Newtonian fluid.

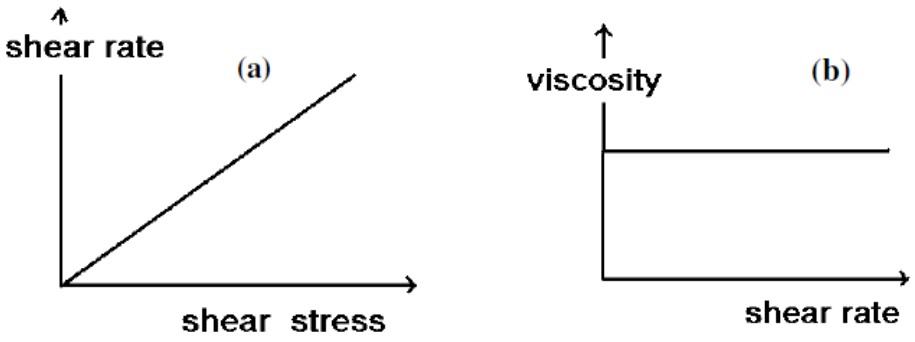


Fig.1.2: Plot of (a) shear rate vs. shear stress (b) shear rate vs. viscosity for Newtonian fluids [14].

So the viscosity of a Newtonian fluid remains constant with varying shear rate at a given temperature. The viscosity is constant with shearing time.

Non-Newtonian Fluid:

A Non-Newtonian fluid is a fluid whose viscosity is dependent on applied stress [14]. Therefore various measurable factors of viscometer, spindle and rotational speed have an impact on the calculated viscosity. This calculated viscosity is known as apparent viscosity. Various types of Non-Newtonian fluids exists which are characterised by how the fluid's viscosity differs with the changing shear rate.

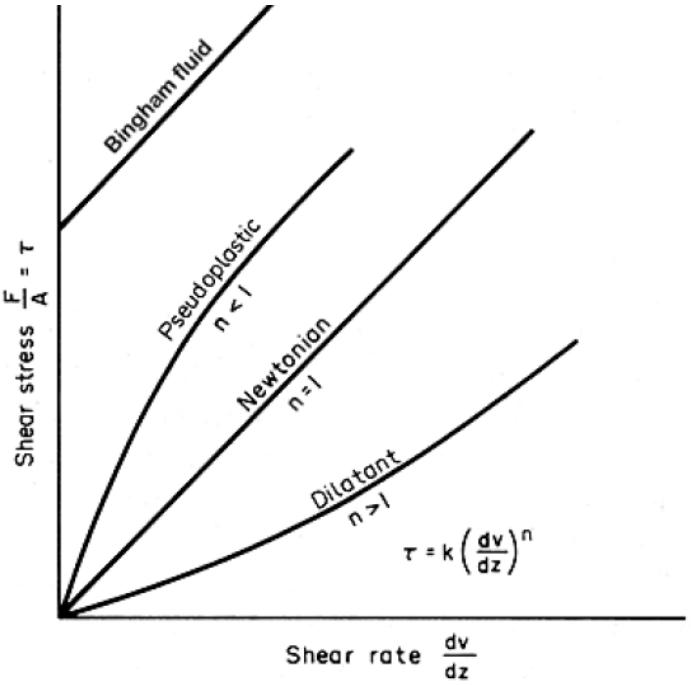


Fig.1.3: Shear Stress vs. Shear Rate [14]

1.5 Starch

Starch is a carbohydrate which contains large number of glucose units which are joined by glycosidic bonds $(C_6H_{10}O_5)_n$. It is mostly found in human diets and is contained in huge quantity in potatoes, wheat, corn, rice and cassava. It is a white, tasteless and odourless powder which is insoluble in cold water [15].

1.6 Types of Starch

Starches contain two molecules -- amylose and amylopectin joined to form starch granules. Amylose and amylopectin exhibit different properties, which characterise the various types of starches.

1.6.1 Corn Starch

Corn starch is obtained from maize grain. It is extracted from the endosperm of the corn kernel. It is used in thickening sauces or soups, and also for preparing corn syrup and other sugars [15].

1.6.2 Potato Starch

Potato starch is extracted from potatoes. It comprises of large oval shaped granules whose size ranges from 5 to 100 μm. Being a very refined starch it comprises of little protein and fat which gives it an explicit white colour along with good clarity, high binding strength and a long texture. It is used for making noodles, bakery cream and also as a thickener, gluing agent etc [15].

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Introduction

The study of the rheological properties of slurries has received a lot of attention in the past because of its wide range of applications. Reducing the slurry viscosity is important for its transportation. Rheological behaviour of the slurry or paste is significant to modify the characteristics of cosmetics, gels, foods etc. Electrolytes are vital in changing their rheological properties. The properties depend on many variables like solid concentration, pH [12], surface charge of the particles [13], exchangeable ions of clay particles, temperature [12].

The interactions between electrostatically charged clay particles and the formation of a gel structure are not only important from a scientific point of view but also technological applications like drilling of mud. These characteristics can be changed to get desired properties by adding electrolytes, polymers, surfactants and organic matter. The effect of cationic surfactants (benzyl dimethyltetradecyl ammonium chloride (BDTAC) and dodecyltrimethyl ammonium bromide (DTAB)) on bentonite clay has been studied [11]. At lower solid concentration (1 or 2 %) they exhibit Newtonian behaviour but flow becomes pseudoplastic at higher solid concentration. D.Penner, G.Lagaly studied the effect of various anions on the rheological properties of sodium montomorillonite suspensions [1]. In 2% sodium montomorillonite dispersions, C_k for sodium chloride and sulphate was higher than C_k in dilute dispersions (0.025%). For Na_2HPO_4, NaH_2PO_4, and H_3PO_4, the opposite was in accordance. The C_k values for the dilute suspensions were 1100, 460, and 32 mmol/l respectively, and for the 2% suspension 80, 40, and 10 mmol/l.

2.2 Studies on the rheology of bentonite clay in presence of Additives

The rheological behaviour of clay particles in the presence of various additive have been studied many a times. The influences of electrolytes, polymers as well as some surfactants on the bentonite-water system have been studied [5]. Rheological properties of Ca-Bentonite and Na-Bentonite were studied after LiCl, KCl, $CaCl_2$, $MgCl_2.6H_2O$ electrolytes; $(NaPO_3)_n$, polyvinyl pyrolidone (PVP) polymers and an anionic surfactant (linear alkyl benzene sulphonate, LABS) were added [4]. The plot shows a linear change of shear stress with shear rate indicating that both the slurries act as Bingham plastics. The plot of apparent viscosity verses shear rate shows a decline at small shear rates which indicates thixotropic nature of the samples. The plot of Ca-Bentonite decreases slowly as compared to Na-bentonite. The Ca-bentonite has a lower apparent viscosity of 2.5 mPa sec compared to Na-bentonite having a higher viscosity of 28 mPa sec.

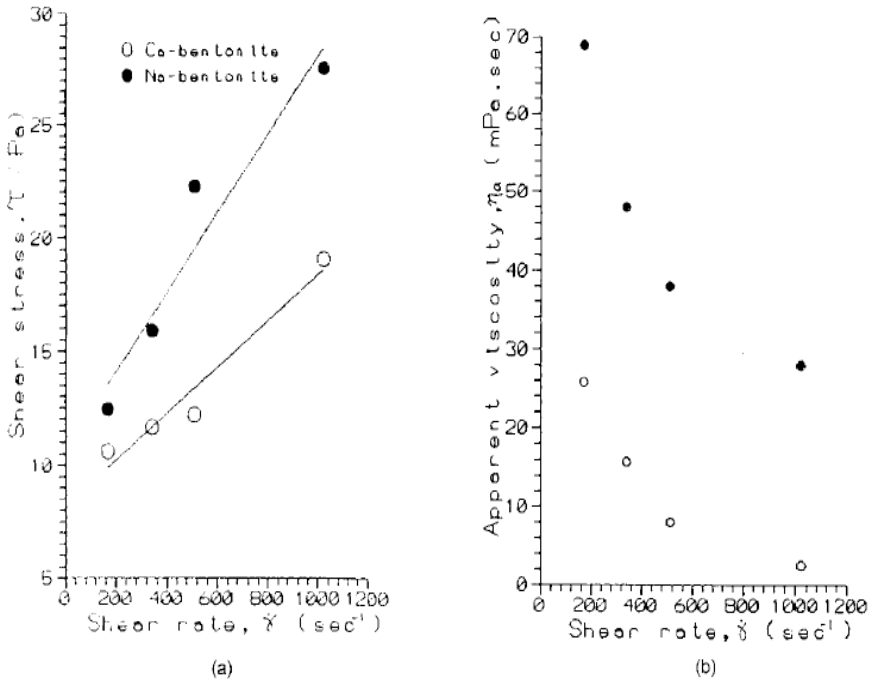


Fig 2.1: (a) The shear stress vs. shear rate rheogram (b) The apparent viscosity vs. shear rate rheogram [4].

Upon addition of LiCl and KCl, there is an initial decrease in viscosity followed by an increase. The Li^+ and K^+ are drawn towards the negative faces of the clay particles and the Cl^- ions drawn towards the positive edges decreasing the net electrostatic interaction between the particles,

thus viscosity decrease. Due to coagulation at increased concentration of salts viscosity again increases. To its contrary Ca^{+2} and Mg^{+2} ions do not neutralise the negative faces whereas Cl^{-} ions are free to neutralise the positive faces. Thus stabilises the particles more and viscosity increases. Upon increased addition due to liquification by anions viscosity decreases.

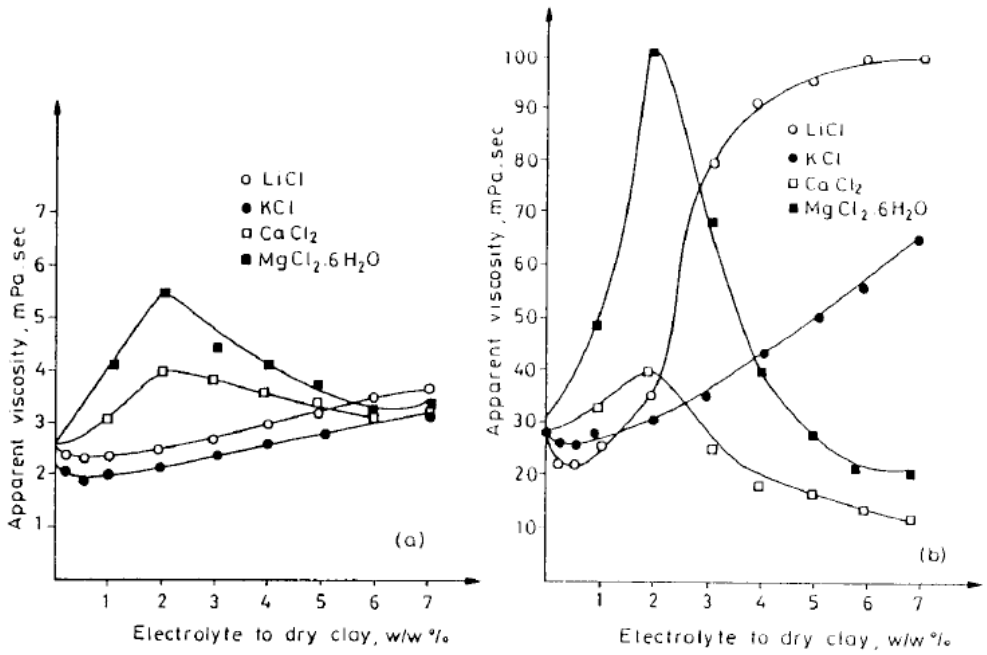


Fig 2.2: (a) The changes of the apparent viscosity of the natural Ca-bentonites (b) The changes of the apparent viscosity of the Na-peptized bentonites [4].

The effect of surfactants on the rheological behaviour of sodium-Bentonite slurries have been studied [9]. It was found that dimethyl ammonium ion got adsorbed on the negetive faces of bentonite at pH values around 2.4 and reduced the charge thereby reducing the face-edge communication and in turn reducing the yield stress. At pH 9.5 the flow values changed with the DDAC concentration. At DDAC concentrations > 10^{-4} the particles settled in the form of flocs because the exchange of the counter ions by DDA^{+} made the particles less hydrophilic.

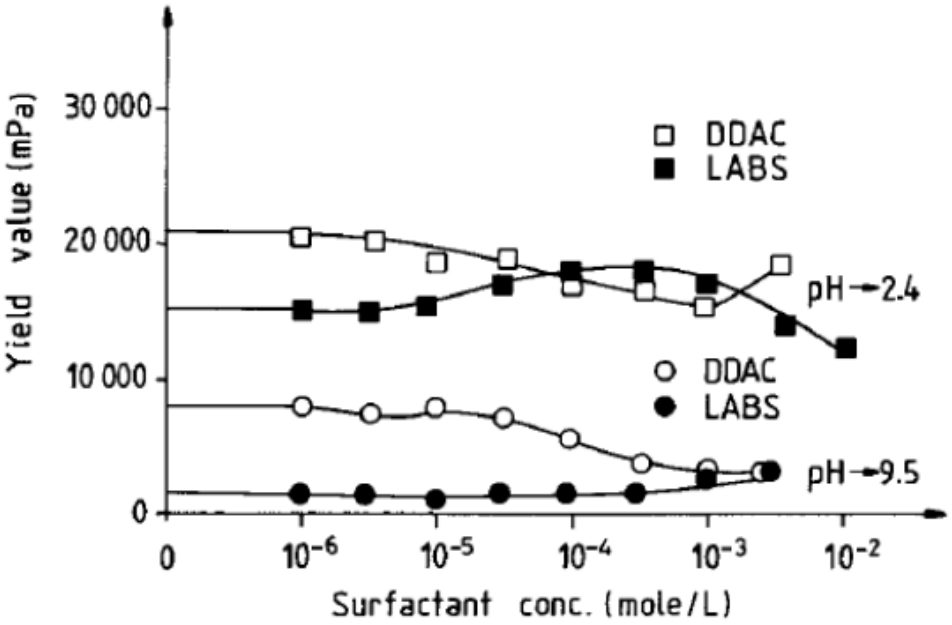
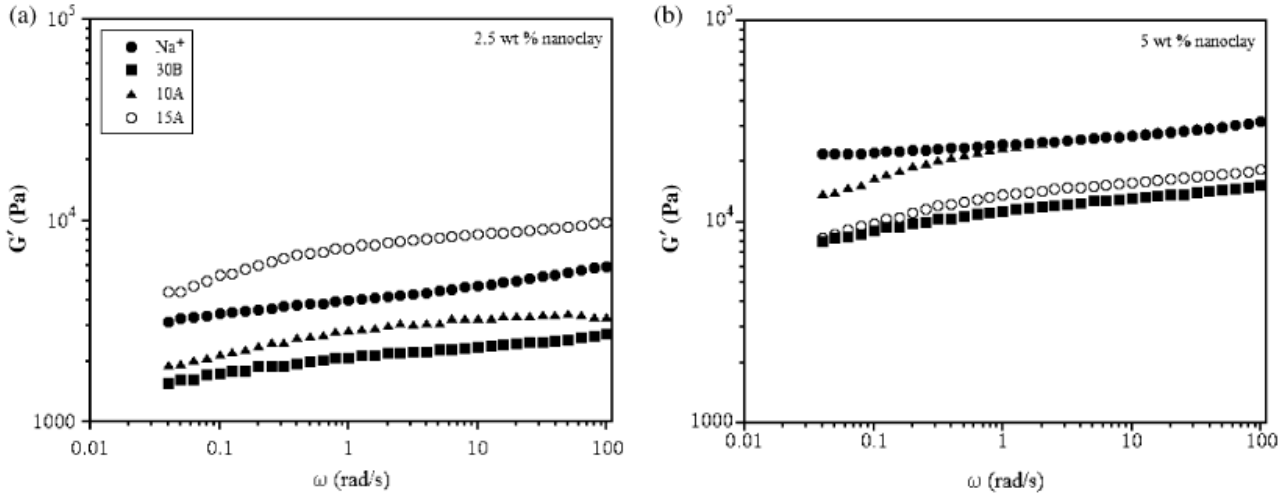


Fig 2.3: Yield value of sodium bentonite slurries (6% w/w) vs. the amount of DDAC and LABS [9].

2.3 Studies on the rheological behaviour of starch-clay mixtures

The rheology of bentonite clays incorporated into wheat, corn and potato starch have been studied [8]. The Cloisite Na^+ displayed gel-like behaviour at higher concentrations of clay. The elastic modulus of the nanoclay samples was plotted verses frequency. Apart from the 2.5 (w/w %) wheat-starch concentration, the Cloisite Na^+ samples showed the highest values for elastic modulus. Also increasing the concentration of Cloisite Na^+ from 2.5 to 10 (w/w %) increased the elastic modulus from around 3000 to 200,00Pa (Bor-Sen Chiou et al.).



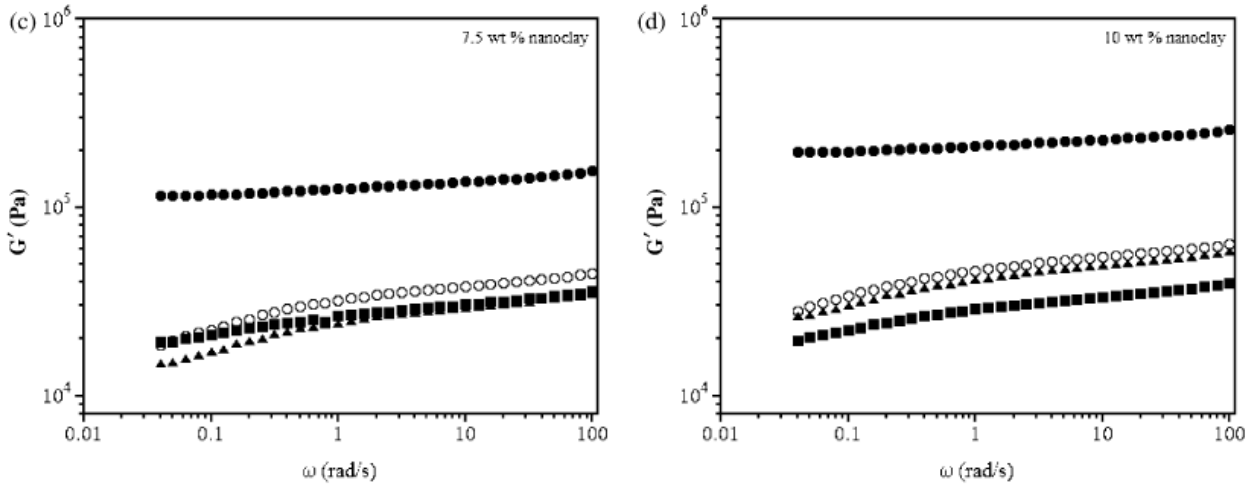


Fig 2.4: Values of Elastic modulus for (a) 2.5 w/w %, (b) 5.0 w/w %, (c) 7.5 w/w %, and (d) 10 w/w % wheat starch–nanoclay samples verses frequency [8].

2.4 Studies on the Rheology of Bentonite Clay in the Presence of Surfactants

The rheological behaviour of bentonite suspensions in the SDS have been studied [9]. The addition of anionic surfactant SDS in different concentrations caused increase in viscosity by penetrating into the inner layer and thereby increasing the mechanical resistance. Also development of steric interaction with clay particles decreased the electrical repulsion because of screening effects. Surfactant's tail gets joined to the head of clay particles forming clusters as a result of electrical aggregation.

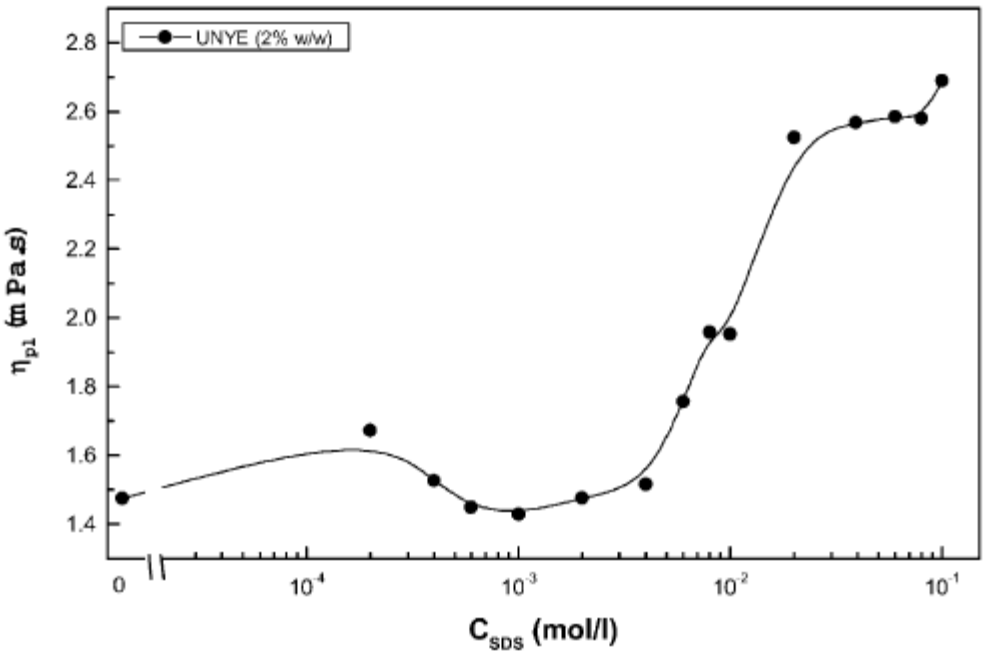


Fig 2.5: Effect of SDS on the viscosity of 2% (w/w) bentonite suspensions [9].

CHAPTER 3

EXPERIMENTAL WORK

3. EXPERIMENTAL WORK

3.1 Materials:

Bentonite was obtained from Merck Chemie Pvt. Ltd., India. The corn starch and potato starch were acquired from Loba Chemie Pvt. Ltd., India. Distilled water of resistivity (18.2 MOhm cm), surface tension (71.5 mN/m) and pH (6.5-7) was used for all the measurements.

3.2 Methods:

CLAY SMAPLE:

Property: method(units)	Bentonite
Mineralogical composition (X-ray diffraction)	89% Montmorillonite, 7% Quartz, 3% Illite trace-Plagioclase
Cation exchange capacity: EPA 9081(meq/100g)	84.1
BET surface area (m^2/g)	27.6
Hydraulic permeability: ASTM D5084 (cm/s)	4×10^{-10}

Analyses performed by IT corporation geotechnical laboratory.

Table 3.1: Analysis of the properties and their values of bentonite clay sample

The bentonite slurry was prepared by dissolving clay particles in distilled water along with vigorous stirring. The slurry volume dispersed at one time was 10 cm^3.

A cone and plate viscometer (BOHLIN VISCO-88, Malvern, U.K.) was used for measuring the viscosity. The conical section has an angle of 5.4° and diameter 30 mm. A gap of 0.15 mm was provided between the cone and plate for all the measurements. The measurements were performed at room temperature. The viscosity of the slurry without starch containing 5%, 6%, 8% and 10% (% by wt.) were evaluated at changing shear rates from 19.34 s^{-1} to 103.16 s^{-1}.The slurry in the presence of starch were prepared by adding desired amount of starch and stirred

vigorously. All the experiments were performed at shear rate of 25.79 s^{-1} for viscosity measurement with respect to time.

Both the corn starch and potato starch were added with the bentonite slurry at four different concentrations of 2%, 4%, 5% and 6%. The viscosity was then evaluated at changing shear rates from 19.34 s^{-1} to 103.16 s^{-1}. Also viscosity vs time was measured for each concentration at a fixed shear rate of 25.79 s^{-1}.

Non-ionic surfactant IGEPAL CO-630 of concentration 10^{-3}M was added to the bentonite slurry with four different corn starch concentrations of 2%, 4%, 5% and 6%. The viscosity was then evaluated at changing shear rates from 19.34 s^{-1} to 103.16 s^{-1}. Also viscosity vs time was measured for each concentration at a fixed shear rate of 25.79 s^{-1}.

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1 Effect of Clay Concentration:

Experiments were performed for four different concentrations (5%, 6%, 8% and 10%) of bentonite-water slurry and viscosity vs shear rate plotted by changing the shear rate from 19.3 to 103.1 s^{-1}. It was established that viscosity reduced with increasing rate of shear. This slurry property is typical of shear thinning behaviour or the bentonite slurry can be concluded to be of pseudoplastic in nature.

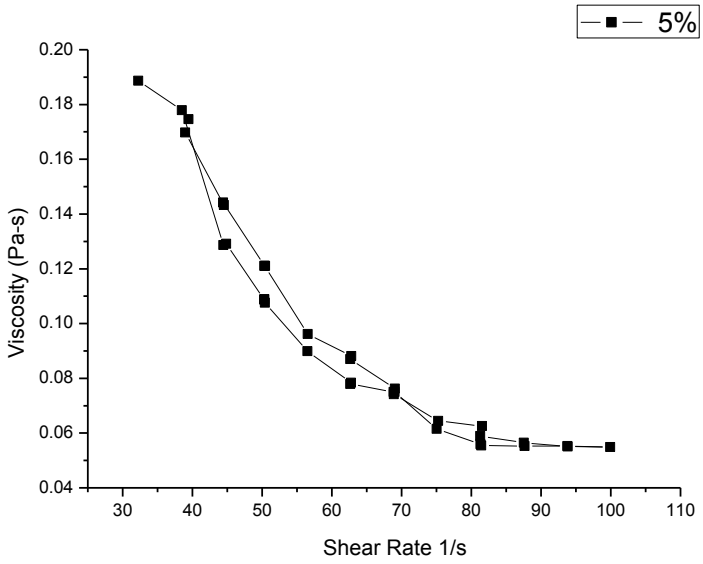


Fig 4.1: Viscosity vs Shear Rate for 5% clay concentration

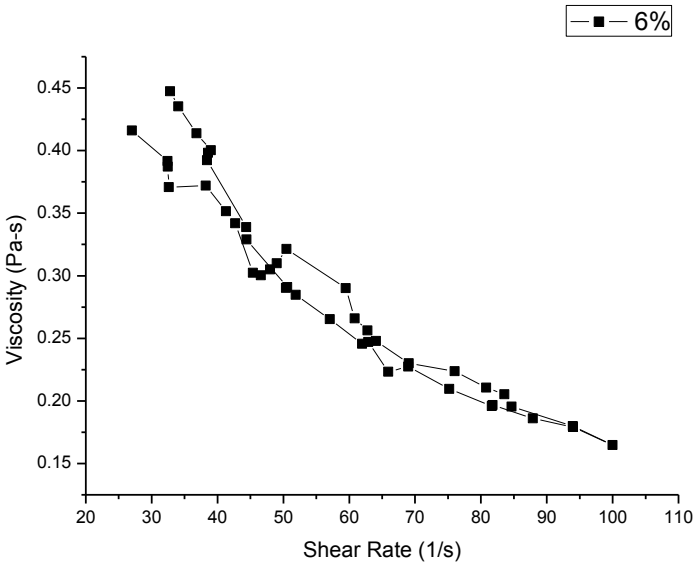


Fig 4.2: Viscosity vs Shear Rate for 6% clay concentration

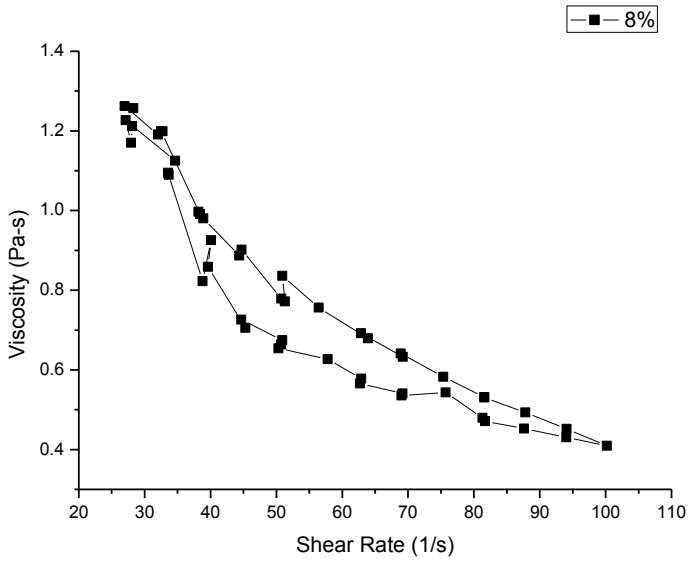


Fig 4.3: Viscosity vs Shear Rate for 8% clay concentration

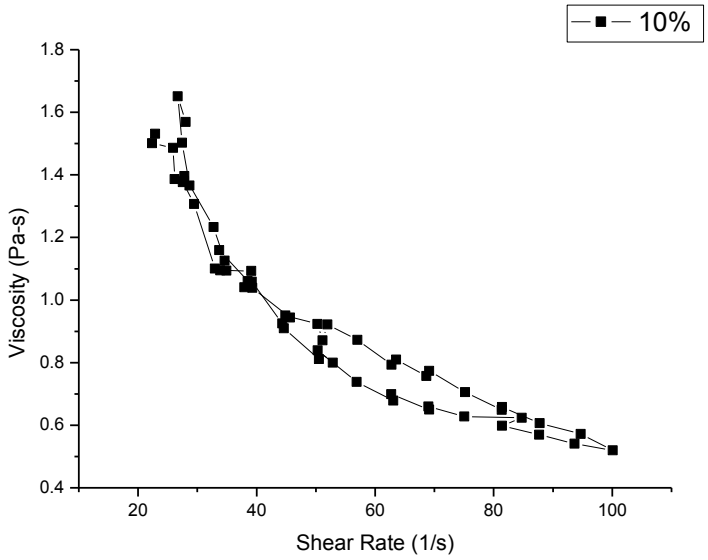


Fig 4.4: Viscosity vs Shear Rate for 10% clay concentration

The viscosities at changing concentration of clay were plotted in Figure 4.2 at 25.79s^{-1} shear rate. It is observed that the viscosity increases nonlinearly with increasing the concentration.

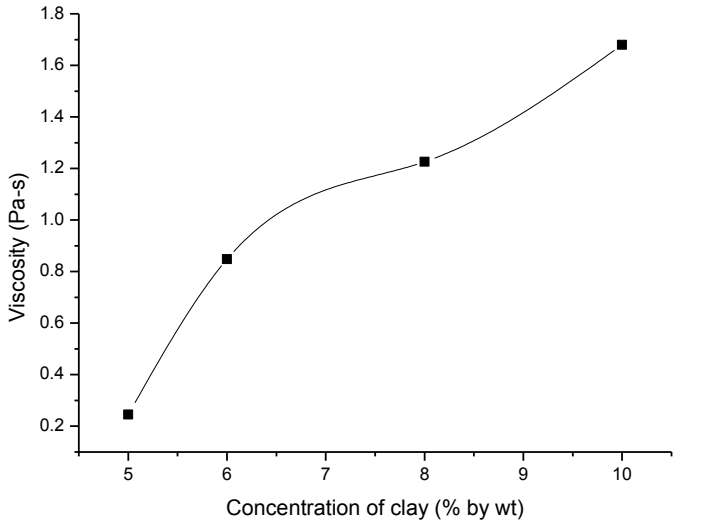


Fig 4.5: Viscosity vs Concentration of clay

4.2 Effect of Adding Corn Starch and Potato Starch

Different concentrations of starch with 8% bentonite clay were taken and the viscosity was measured at varying shear rates (19.3s^{-1} to 103.1s^{-1}). Figure 4.6, 4.7, 4.8, 4.10, 4.11 and 4.12 shows the viscosities obtained when operating at increasing shear rate for different starch concentration (2%, 4% and 5%). The average viscosities obtained were also plotted with concentration in Figure 4.9 and Figure 4.13.

It was observed that the addition of starch caused a decrease in viscosity making the clay more pseudoplastic in nature. This behaviour can be attributed to the mineral composition of starch powders and surface charge developed after dispersion. Another reason could be the reduction in the free liquid for dispersion and the attached liquid wetting on the surface of the starch granules.

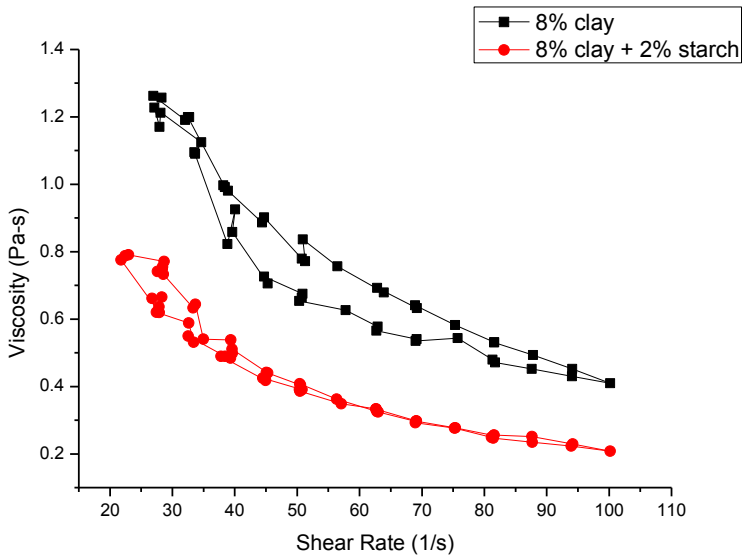


Fig 4.6: Viscosity vs Shear Rate for 2% concentration of corn starch

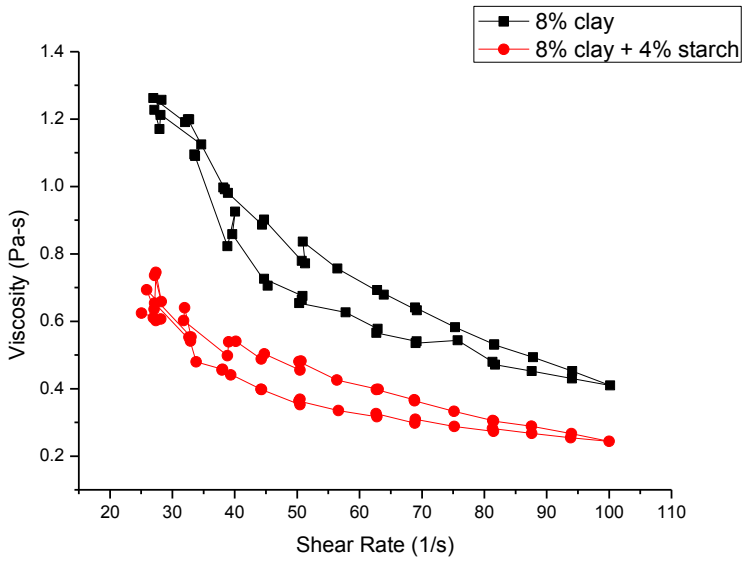


Fig 4.7: Viscosity vs Shear Rate for 4% concentration of corn starch

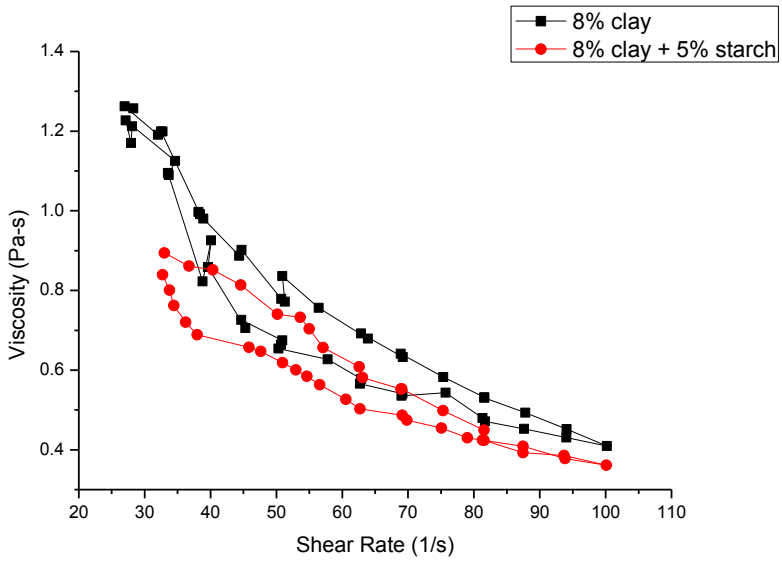


Fig 4.8: Viscosity vs Shear Rate for 5% concentration of corn starch

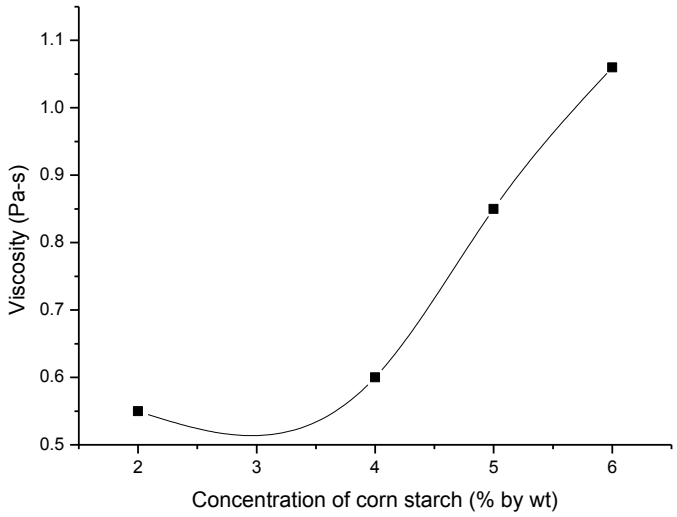


Fig 4.9: Viscosity vs Corn starch concentration

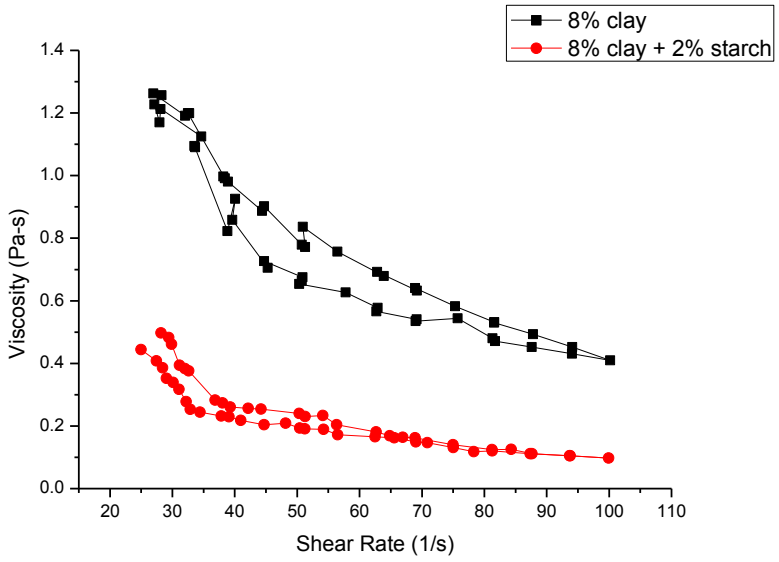


Fig 4.10: Viscosity vs Shear Rate for 2% concentration of potato starch

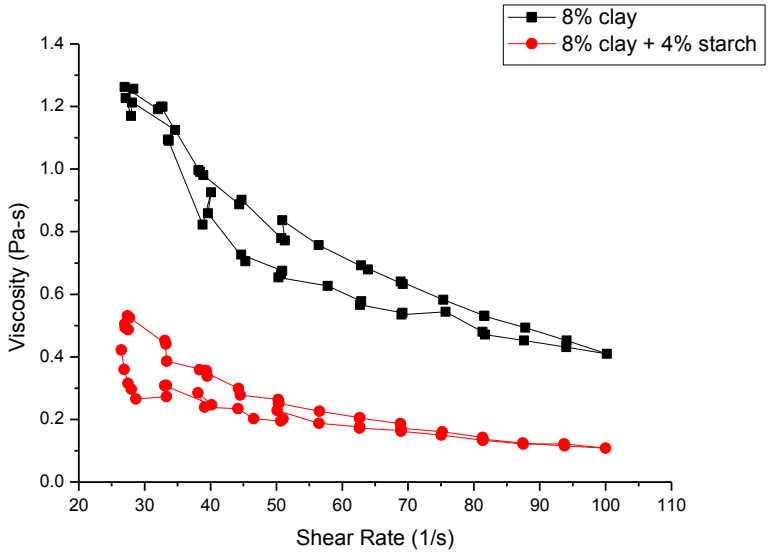


Fig 4.11: Viscosity vs Shear Rate for 4% concentration of potato starch

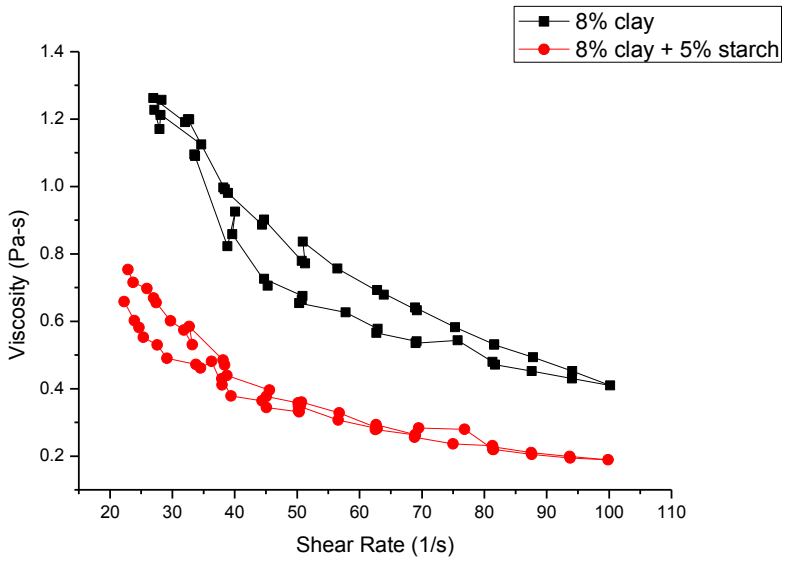


Fig 4.12: Viscosity vs Shear Rate for 5% concentration of potato starch

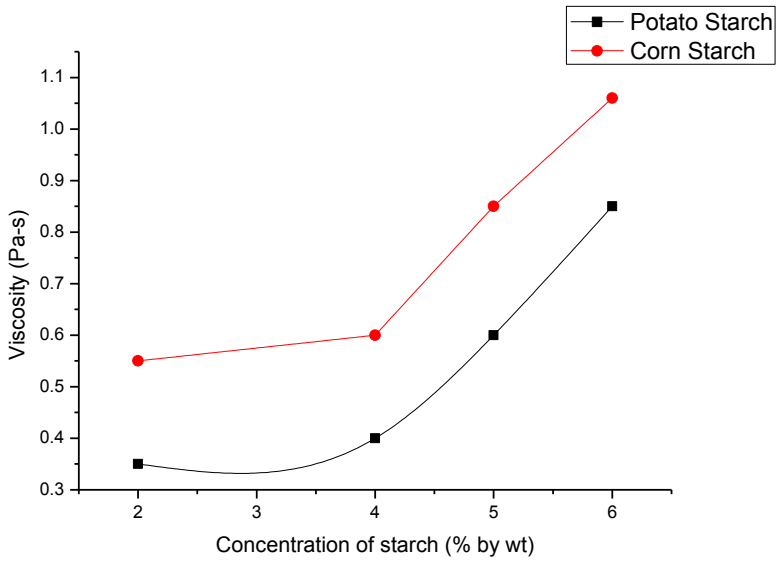


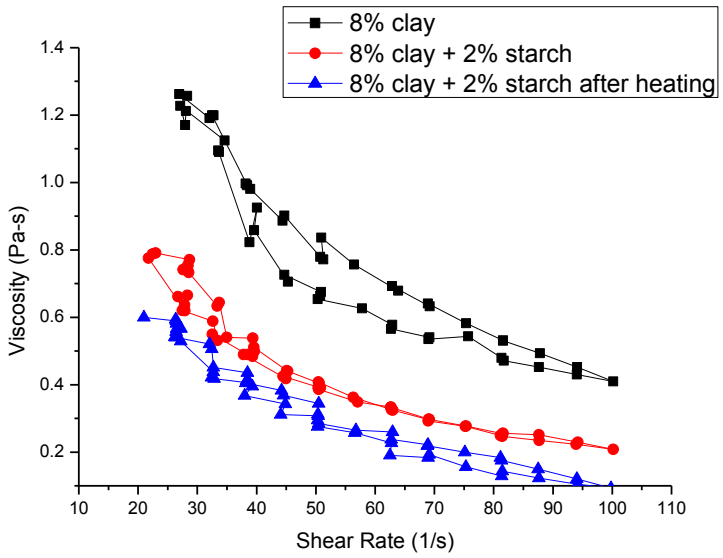
Fig 4.13: Viscosity vs Starch concentration

4.3 Effect of Heating

The bentonite-starch slurry with different starch concentration (2%, 4% and 5%) were heated using a REMI heater at about 200°c for about 20 minutes. Then the viscosity measurement was done for each concentration of corn and potato starch at varying shear rate($19.3s^{-1}$ to $103.1s^{-1}$). Figure 4.14 shows the viscosities obtained when operating at increasing shear rate. The average viscosities obtained were also plotted with concentration in Figure 4.15.

It was observed that the viscosity reduced after heating for every concentration of starch. This reduction in viscosity can be attributed to various reasons like reduction in the degree of hydration of the counter ions, reduction in the viscosity of the suspending medium, increased dispersion of the clay particles and also their increased thermal energy. At high temperatures the clay particles degrade, they start to dehydrate resulting in low rheological properties.

The effect of temperature seems different for different concentration of starch. This can be connected to the volume fraction of swollen particles as well as their deformability. Higher deformability leads to lower rigidity resulting in decreased viscosity.



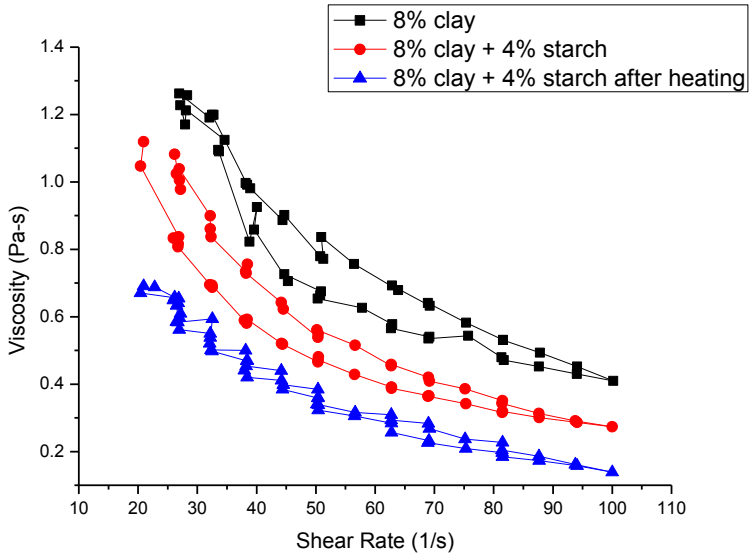


Fig 4.14: Viscosity vs Shear Rate for 2% and 4% concentration of corn starch

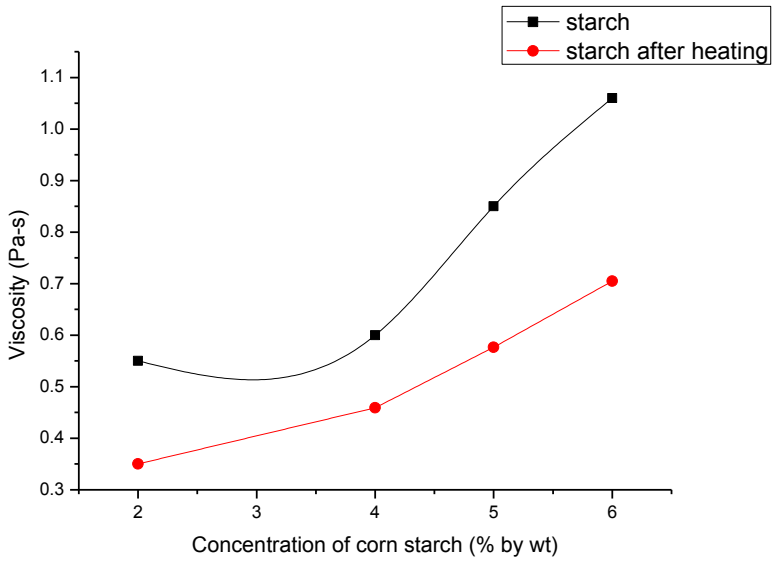


Fig 4.15: Viscosity vs Corn starch concentration

4.4 Effect of Surfactant (IGEPAL-CO630)

Different concentrations of corn starch and 8% bentonite suspension with non-ionic surfactant (IGEPAL-CO630) of concentration 10^{-3}M were taken and the viscosity was measured at varying shear rates (19.3s^{-1} to 103.1s^{-1}). Figure 4.16 shows the viscosities obtained when operating at increasing shear rate for different starch concentration (2%, 4% and 5%). The average viscosities obtained were also plotted with concentration in Figure 4.17.

It was observed that the addition of surfactant caused the viscosity to decrease. This behaviour can be attributed to the adsorption of the surfactant molecules on the surface of clay particles. The clay particles with adsorbed surfactant molecules would repulse more due to steric repulsion. The negatively charged active groups of surfactant gets attached to the positively charged surface edges forming a new cluster structure which lowers the viscosity.

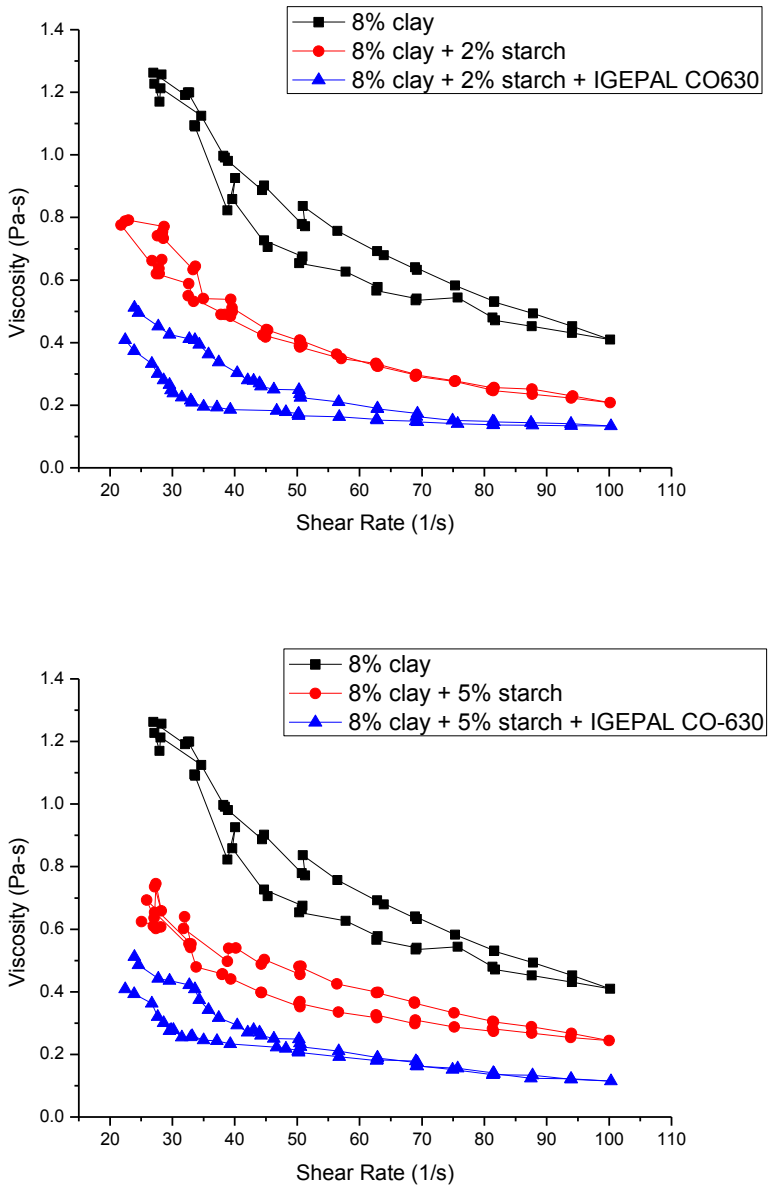


Fig 4.16: Viscosity vs Shear Rate for 2% and 5% concentration of corn starch after addition of 10^{-3}M IGEPAL-CO630

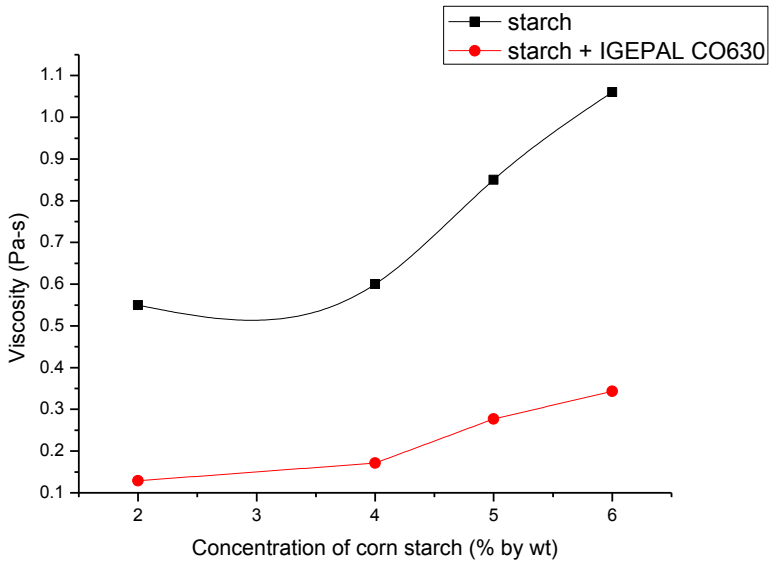


Fig 4.17: Viscosity vs Corn starch concentration after addition of 10^{-3}M IGEPAL-CO630

CHAPTER 5

CONCLUSION

5. CONCLUSION

It is remarked that viscosity of the bentonite slurry increased with the concentration of solid content. The change in starch content and the adsorption of IGEPAL-CO630 changed the surface charge of bentonite suspension. With the starch addition the viscosity decreased due the reduction in the free liquid for dispersion and the attached liquid wetting on the surface of the starch granules. The adsorption of non-ionic surfactant increased the steric repulsion which lowered the viscosity. It was also remarked that heating reduced the viscosity due to increased thermal energy and dehydration of clay particles.

CHAPTER 6

REFERENCES

6. REFERENCES

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